

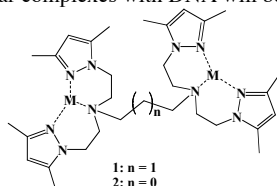
**Induction of Z-DNA:  
When Similar Dinuclear Complexes interact differently with DNA**

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During our studies aimed at better understanding the factors which influence the formation of the left-handed Z-DNA,<sup>[1]</sup> we speculated that dinuclear metal complexes might induce Z-DNA more efficiently than their mononuclear analogues.<sup>[2]</sup>

Our aim is to introduce the new family **1** of homodimetallic complexes. They are based on **2** (M = Cu<sup>2+</sup> and Ni<sup>2+</sup>) published by Reedijk *et al.*<sup>[3,4]</sup> The interaction of **1** and **2** (M = Cu<sup>2+</sup> and Ni<sup>2+</sup>) with poly d(GC) has been examined. Furthermore, this allowed to study the influence of the intermetallic distance between the metal centers concerning the transition from B- to Z-DNA. Surprisingly, **1** and **2** (M = Cu<sup>2+</sup> and Ni<sup>2+</sup>) showed different interactions as only **1** induced Z-DNA. These unexpected variations in reactivity of structurally very similar complexes with DNA will be discussed.



[1] B. Spingler, *Inorg. Chem.* **2005**, *44*, 831.

[2] B. Spingler, C. Da Pieve, *Dalton Trans.* **2005**, 1637.

[3] W. L. Driessen, W. G. Haanstra, J. Reedijk, *Acta Cryst.* **1992**, *C48*, 1585.

[4] N. Veldman, A. L. Spek, G. Tabbi, W. L. Driessen, J. Reedijk, *Acta Cryst.* **1996**, *C52*, 2698.

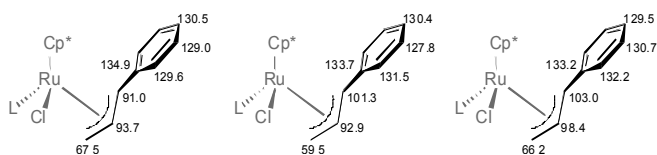
**NMR and X-ray studies on a Ru(IV) allyl complex.  
An explanation for the observed regioselectivity.**

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The use of ruthenium based catalysts in allylic alkylation and amination processes, affords primarily branched organic products due the preferred attack at the more substituted carbon.

Here we report NMR and X-ray studies, which together with computational data give an explanation of the observed high branched-to-linear regioselectivity. The oxidative addition of cinnamyl chloride with [Cp\*<sub>2</sub>Ru(L)<sub>3</sub>] (L = CH<sub>3</sub>CN) in dichloromethane solution, gives three ruthenium (IV) isomeric complexes. The <sup>13</sup>C NMR data for the allylic moieties are shown in the figure.



The NMR data reveal a marked difference between the carbon chemical shifts of the allylic termini in the three complexes. The X-ray structure and computational data show clearly different terminal Ru-C bond distances. These results provide an explanation for the observed control of regioselectivity.

[1] Hermatschweiler, R.; Fernández, I.; Pregosin, P. S.; Watson, E. J.; Albinati, A.; Rizzato, S.; Veiros, L. F.; Calhorda, M. J. *Organometallics* **2005**, *24*, 1809-1812.

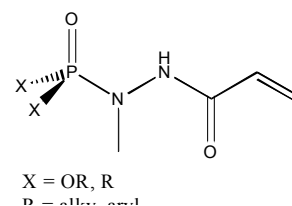
**New Phosphorus containing Flame Retardants for Cotton**

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There exist few commercially available flame retardants for cotton. All of these retardants contain phosphoorganic compounds and further additives. Other phosphorus based flame retardants have been synthesized, but are not commercially employed due to toxicological properties or cost.

Here we present a new type of phosphorus containing compounds which we can polymerize onto cotton fabrics to impart flame retardant properties.



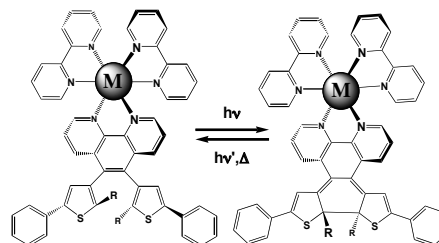
The characterization of the treated fabrics was performed by IR-ATR, SEM, TGA, the flame retardant properties were evaluated by limiting oxygen index (LOI) test, and the durability of the surface modification was checked by different washing cycles.

**Photochromic Dithienylethene-Phenanthroline Hybrid System Containing Ru(II), an Opportunity to Increase Photofatigue Resistance**

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In this work, we have developed a system, in which a photochromic unit (dithienylethene<sup>[1]</sup>) has been combined with Ru(II) metal complex.<sup>[2]</sup> By irradiation at 450 nm into the MLCT band of the metal complex, a photosensitized cycloreaction takes place. This low energy light, used to perform the electrocyclic reaction, allows an increase of photofatigue resistance.



If light of 254 nm wavelength is used to close the molecule, after a few cycles, the photochromic properties disappear. On the other hand, irradiation at 450 nm, the photochromic properties remain unchanged.

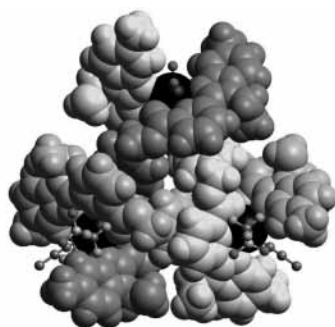
The authors thank the Swiss National Science Foundation for financial support.

[1] Irie M., *J. Org. Chem.*, **2002**, 4574.

[2] Vivian Wing-Wah Yam, *J. Am. Chem. Soc.*, **2004**, 12735.

**Isolation and characterization of the first circular single-stranded poly-metallic lanthanide-containing helicate**Jean-Michel Senegas,<sup>a</sup> Sylvain Koeller,<sup>a</sup> Gérald Bernardinelli<sup>b</sup> and Claude Piguet<sup>\*a</sup><sup>a</sup>Department of Inorganic Chemistry, University of Geneva, 30 quai E, Ansermet, CH1211 Geneva 4, Switzerland.<sup>b</sup>Laboratory of X-ray Crystallography, University of Geneva, 24 quai E. Ansermet, CH-1211 Geneva 4, Switzerland

A thorough examination of the disassembly of bimetallic triple-stranded lanthanide helicates  $[\text{Ln}_2(\text{Li})_3]^{6+}$  in excess of metals shows the competitive formation of standard linear bimetallic complexes  $[\text{Ln}_2(\text{Li})_2]^{6+}$ , and circular trimetallic single-stranded helicates  $[\text{Ln}_3(\text{Li})_3]^{9+}$ .



[1] Jean-Michel Senegas, Sylvain Koeller, Gérald Bernardinelli and Claude Piguet, *Chem. Commun.*, **2005**, 2235-2237.

**The Cyanobacterial Iron Chelator Anachelin – From Fe(III) Binding to Surface Binding**Karl Gademann\*, Yann Bethuel\*, David Wäckerlin<sup>‡</sup>, Barbora Malisova<sup>‡</sup>, Samuele Tosatti<sup>‡</sup>, Stefan Zürcher<sup>‡</sup> and Marcus Textor<sup>‡</sup>

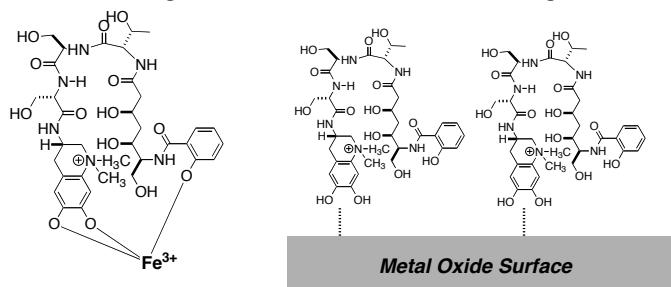
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Cyanobacteria evolved sophisticated strategies for iron acquisition, transport and storage. The iron chelator anachelin[1] was evolutionarily optimized to effectively bind to Fe(III) ions. We wondered whether this exceptional phenomenon could be applied to bind to *metal oxide surfaces*.

**Ion Binding**

vs.

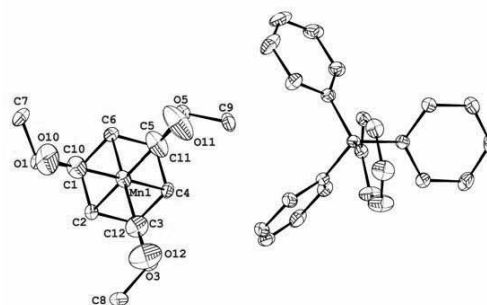
**Surface Binding**

We will present a biomimetic approach for surface modification utilizing tailor-made anachelin derivatives. The generation of self-assembled monolayers and their potential applications are discussed.

[1] For our own efforts in this area, see: K. Gademann, *ChemBioChem* **2005**, *6*, 913; K. Gademann, Y. Bethuel, *Org. Lett.* **2004**, *6*, 4707; K. Gademann, Y. Bethuel, *Angew. Chem., Int. Ed.* **2004**, *43*, 3327; K. Gademann, H. Budzikiewicz, *Chimia* **2004**, *58*, 212.

**Ion Pairing on  $[(\eta^6\text{-Arene})\text{Mn}(\text{CO})_3]^+[\text{X}]^-$  Complexes**Danièle Schott,<sup>a</sup> Paul S. Pregosin,<sup>a\*</sup> Béatrice Jacques,<sup>b</sup> Murielle Chavarot,<sup>b</sup> Françoise Rose-Munch<sup>b\*</sup> and Eric Rose.<sup>b</sup> schott@inorg.chem.ethz.ch<sup>a</sup>Laboratory of Inorganic Chemistry, ETHZ, Hönggerberg CH-8093 Zürich, Switzerland; <sup>b</sup>Laboratoire de Chimie Organique, UMR 7611, Université P. et M. Curie, 75252 Paris Cedex 05, France.

Significant differences in the ion pairing were found in a series of salts  $[(\eta^6\text{-Arene})\text{Mn}(\text{CO})_3]^+[\text{X}]^-$  where the counter ion, X, is either  $\text{BPh}_4^-$  or  $\text{BARF}^-$ .



PGSE diffusion measurements in different solvent and NOESY Spectra for those anions confirm these observations, providing unexpectedly strong ion pairing for  $[(\eta^6\text{-Arene})\text{Mn}(\text{CO})_3]^+[\text{BPh}_4]^-$  in  $\text{CD}_2\text{Cl}_2$ .

**Enantioselective Hydrogen Transfer Reactions Catalyzed by Ruthenium(II) Amino Alcohol Complexes Attached to  $\beta$ -Cyclodextrin**

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We have synthesized new water-soluble Ru complexes of  $\beta$ -cyclodextrin-modified amino alcohols to serve as supramolecular catalysts in hydrogen transfer reactions in the presence of formate. The reduction of aromatic and, for the first time, of aliphatic, unconjugated ketones was accomplished with ee-values as high as 97% in good to excellent yields. In all cases,  $\beta$ -cyclodextrin plays an important role on enantioselection through preorganization of the substrates in the hydrophobic cavity, see example below.

